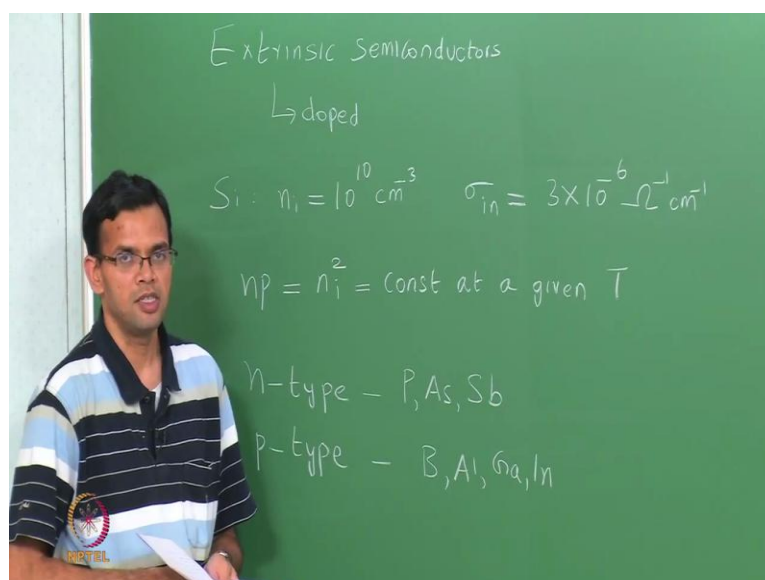


Fundamentals of electronic materials, devices and fabrication
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Lecture - 07
Extrinsic semiconductors-Fermi level

Let us start with a brief recap of last class. Last class, we looked at Extrinsic Semiconductors and another name for these are doped semiconductors.

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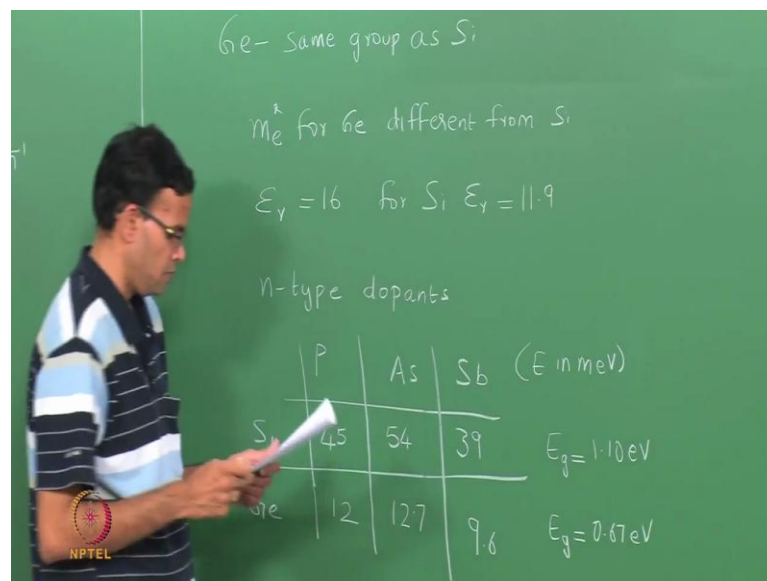


Now, the reason why we wanted to dope was, because we found out that if we had an intrinsic or a pure semiconductor, the carrier concentration at room temperature was very small. Correspondingly, the conductivity was also small. For example, in the case of silicon, we found that the room temperature carrier concentration in an intrinsic semiconductor was only 10^{10} cm^{-3} and the corresponding conductivity is very low, was around $3 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. So, we wanted to increase the conductivity. So, we selectively added impurities or dopants to the silicon in order to make it an extrinsic semiconductor. We also saw that in any semiconductor the law of mass action must always be satisfied so that $np = n_i^2$, which is a constant at a given temperature. This meant that could we can either increase the concentration of electrons or increase the concentrations of holes, we cannot do both.

So, we also saw that there were 2 types of dopants; one was your n-type, the other was the p-type. We saw that in n-type dopant was found in the case of silicon by adding group V elements. The typical elements that we add are Phosphorous, Arsenic, Antimony all of these have 1 extra electron compared to the silicon atom which means you have 1 extra electron in the conduction band, so these are n-type. Similarly, we saw that we could form p-type by doping with group 3 – Boron, Aluminum, Gallium, Indium. These form energy states that are close to the conduction band in the case n-type or close to the valence band in the case p-type, so that these are ionized at room temperature.

So, let us look some more today on the properties of Extrinsic Semiconductors. So far you only talked only about silicon, so what about other semiconductor materials and doping in them?

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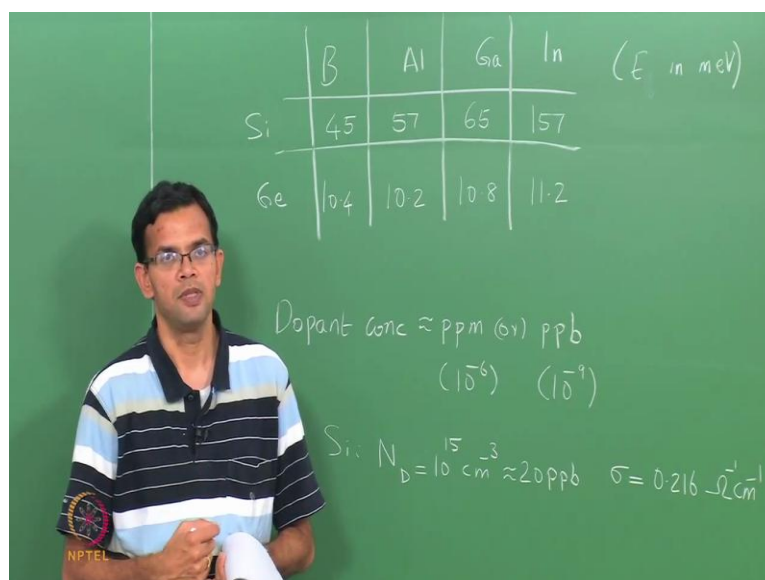


If we look at Germanium, Germanium lies in the same group as silicon, which means all the elements that we used as dopants for silicon could also be used for germanium. So, we can use your group 5 elements like phosphorous or arsenic has an n-type dopant, could also use your group 3 elements like boron as a p-type dopant. Once again in the case of germanium, we can calculate the ionization energies for these dopants, we could use the hydrogenic model; to only difference is the effective mass m_e^* for germanium will be different from that of silicon and similarly, your relative permittivity for germanium, the value is around 16 while for silicon ϵ_r is around 11.9, but we can use the

same hydrogenic model in order to calculate the ionizations energies.

So, let us look at some actual values in just to compare silicon and germanium. Let us look at n-type – Phosphorus, Arsenic and Antimony are the 3 dopants; Silicon and Germanium. If we fill in the numbers, in the case of silicon, we found out that the ionization energy in milli-electron volts. So, energy is in milli-electron volts was around 45, 54, 39. Similarly, in the case of germanium, we will find that the ionization energies are very small. So, this is around 12, 12.7, 9.6. If you remember the band gap of germanium is also smaller, so at room temperature E_g for silicon is around 1.10 electron volts, E_g for germanium is around 0.67 electron volts.

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	B	Al	Ga	In	(E in meV)
Si	45	57	65	157	
Ge	10.4	10.2	10.8	11.2	

Dopant conc \approx ppm (or) ppb
 (10^6) (10^9)

Si: $N_D = 10^{15} \text{ cm}^{-3} \approx 20 \text{ ppb}$ $\sigma = 0.216 \text{ } \Omega^{-1} \text{ cm}^{-1}$

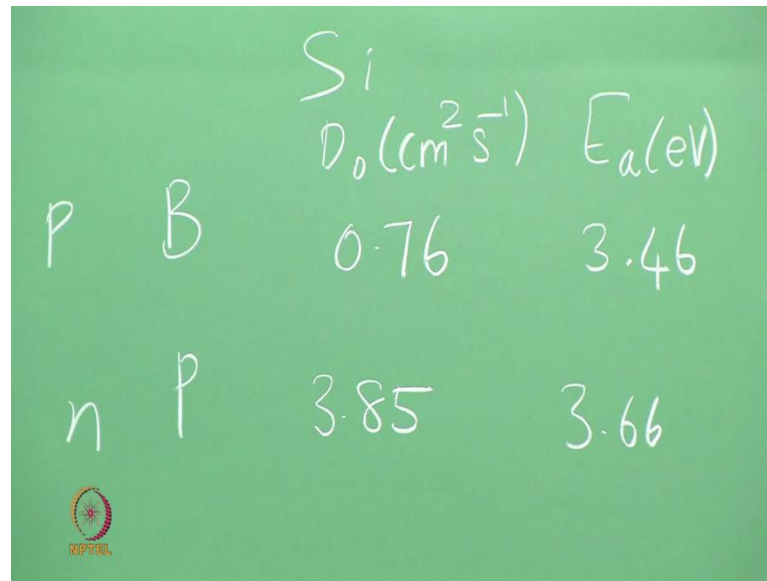
You can do same thing with p-type impurities or p-type dopants – Boron, Aluminum, Gallium and Indium. So, once again let me write silicon germanium 45, 57, 65, 157. Again, if we are writing energy in milli-electron volts, germanium is around 10.4, 10.2, 10.8, 11.2. So, what this means is whether you have silicon or you have germanium both lie in the same group. So, you can dope both of them in a similar fashion. If you want an n-type dopant, you are going to add group V elements; if you want add p-type dopants, you are going to add group 3 elements. Usually, the dopant concentration is very small; we saw earlier in the case silicon that your typical dopant concentration was around parts per million or parts per billion. So, parts per million is 10^{-6} , parts per billion was 10^{-9} . And, even the small amount was enough to increase conductivity by orders of

magnitude.


So, we saw for silicon, if I had an n-type dopant with 10^{15} cm^{-3} which was approximately 20 parts per billion, your conductivity sigma went up to around $0.2 \Omega^{-1} \text{ cm}^{-1}$. One thing we have not look much is how we actually do the doping. So, later when we look at the fabrication part, we will spend some more time on how we actually dope. But, if you think of a parallel to metallurgy one way we can think of is in the case of stainless steel or in the case steel we do something called Carbonizing, where we increase the carbon content. So, it typically what we do is we have your sample at high temperature, you have a carbon source so that the carbon then just defuses into the surface and into the bulk of your steel.

So, we can do something similar in case of doping in semiconductor as well. So, you if want to dope n-type, you have a source of your n-type material, this could be in the gas phase, this could be ion implanted on to the surface, we will see what ion implantation is later, so that these can then defused into the surface, and from the surface in the bulk. If you want to do compensation doping, we saw compensation doping last class where you start with an n-type semiconductor and then you make it p-type by adding excess dopants of the other type. Similarly, in the case compensation doping could take a small portion of your sample that is typically n-type and add excess of p-type. So, it could add excess of boron and then make it a p-type semiconductor. These dopants are usually very stable at room temperature.

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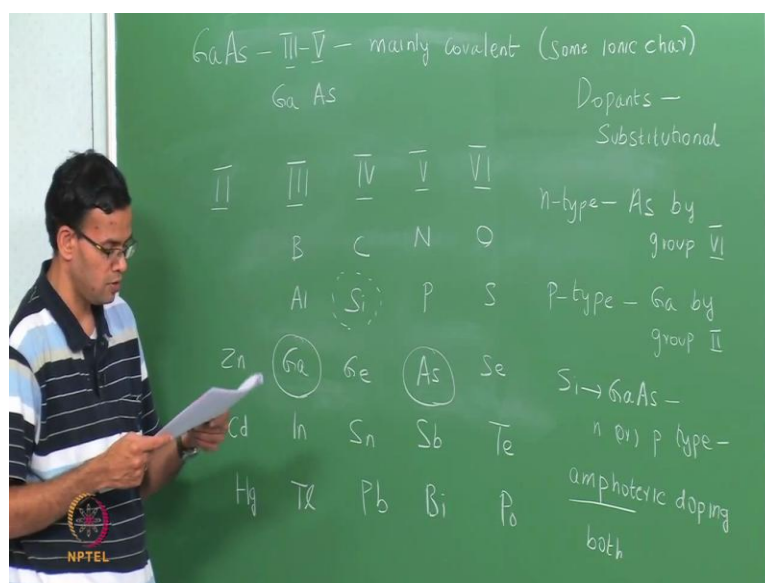


		Si	$D_0 (\text{cm}^2 \text{s}^{-1})$	$E_a (\text{eV})$
p	B		0.76	3.46
n	P		3.85	3.66



Just to give you some numbers. Let us take the case of silicon; I have 2 dopants; one is Boron, one is Phosphorous. Boron is a p-type, Phosphorous is n-type. We can have we will write down the values for the activation energy and diffusion co-efficient for these dopants. So, if I write D_0 and E_a , E_a is the activation energy for diffusion and D_0 is a diffusion constant. So, in the case of boron D_0 has a value for 0.76, activation energy is around 3 and half electron volts; phosphorous is 3.85, E_a is around 3.6 electron volts. What this means is in order to have boron or phosphorous diffusing into a material, you essentially need a high temperature process. The corollary of this is that at room temperature your doping concentrations are inherently very stable in the case of silicon. So, So far you have seen 2 semiconductors silicon and germanium. You have looked at some examples of dopants, calculated the ionization energies. Since, both silicon and germanium belong to the same group, we essentially use the same elements. Things become a little more complicated when we look at other semiconductors.

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So, let us look first at Gallium Arsenide. We saw earlier that gallium arsenide is an example of III-V compound semiconductor. So, gallium is from group III, arsenic is from group V. The bonding in gallium arsenide is mainly covalent, but you also have some ionic character to the bond. Instead of gallium arsenide, if you have something like zinc oxide which is II-VI semiconductor, there will be a higher character as compare to III-V. So, it is also possible to dope gallium arsenide, but they are now more possibilities in this case. To understand this, let us go back to the periodic table, specially the portion around gallium arsenide. So, let me write the periodic table we have done this earlier when we looked at elemental and compound semiconductors. So, group II, III, IV, V and VI – Boron, Carbon, Nitrogen, Oxygen, Aluminum, Silicon, Phosphorous, Sulphur, Zinc, Gallium, Germanium, Arsenic Selenium, Cadmium, Indium, Tin, Antimony, Tellurium, Mercury, Thallium, Lead, Bismuth and Polonium. So, this is just the portion of the periodic table around groups III and V.

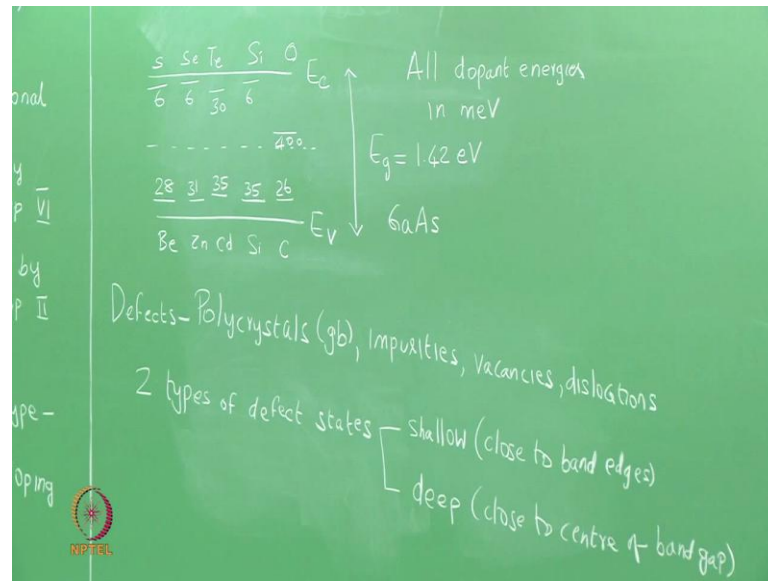
So, the semiconductor we have is gallium arsenide and we want to know what sort of elements could be added as dopants to gallium arsenide to make it p or n-type. So, when we think of dopants, these are usually substitutional which means I am going to replace either gallium or the arsenic atom. So, let us say I want make an n-type gallium arsenide, so I would typically choose elements from group IV, because these elements have one more electron is compared to arsenic. So, if an element from group VI replaces arsenic, we will have one extra electron and if this extra electron is in a shallow state, if it is

easily ionisable, it can get ionized to the conduction band and be available for conduction. So to form n-type, we are going to replace arsenic by group VI. We can use the same argument if you want to make a p-type semiconductor. So, we replace gallium by any of the group twos, which has one less electron or you have one hole. So, there will make it a p-type. If you want make something p-type, we can replace gallium by group two.

Question is what happens if you have a group four impurity. Let us say I have silicon, now silicon is an impurity in gallium arsenide. So, the essentially two possibilities; the silicon can replace the gallium, the silicon can replace the arsenic, and depending on that we can either get an n-type or a p-type. So, if the silicon replaces the gallium and silicon has one more electron because this is group four, this is group three, so the extra electron is available for conduction, it will make it n-type. On the other hand, if silicon replaces arsenic, it has one less electron and it will make it p-type. So, silicon added to gallium arsenide can be either n or p-type, and this type of doping is called Amphoteric doping.

This term Ampho essentially means both means you have the same element. It can act both as an n-type or as an p-type dopant. The only issue here it is really hard to control the position of silicon; it is very hard to get silicon to selectively dope into gallium or to selectively dope into arsenic. So, if we have silicon as a dopant, it is very hard to control the type of dopant and the concentration of dopants. So, we saw that these are all the possible elements that can be used to dope gallium arsenide, the only other question is where are the energy levels located.

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Now, let me just do that by drawing the band gap of gallium arsenide. So, this is my conduction band that is my valence band, the difference between the conduction band and the valence band is your band gap. In the case of gallium arsenide, the band gap is 1.42 electron volts; also mark the center of the gap. So, if you look at the various elements the group II and the group VI elements, these will essentially form impurity states in the band gap of gallium arsenide. And, depending upon whether they are n-type or p-type there will be located either close to the conduction band edge or the valence band edge.

So, if you look at the group VI elements these are n-type. So, this one is sulphur; selenium is also very similar; tellurium is here. Again all the dopant energies are in milli-electron volts, which means the diagram is not really to scale, but we will just show it semi qualitatively, so we have rough idea. Silicon, we said silicon can go either to gallium or to arsenic. So, silicon as an n-type is around 6 milli e v, oxygen on the other hand is around 400. Similarly, we can look at the group II elements, so we have beryllium it is around 28, zinc is 31, cadmium is slightly higher 35. We can also have silicon as a p-type that is around 35 again, carbon is around 26. So, if we have gallium arsenide depending upon the type of impurity, we can either have both n-type and p-type. Similarly for other II-V semiconductors can once again have doping by choosing the appropriate group II or group VI materials.

If you have a II-VI semiconductor something like zinc oxide or cadmium sulphide or cadmium selenide, similarly we can choose appropriate dopants to get both n-type and p-type. Most of what we have done here, so whether we are talking about silicon or germanium or gallium arsenide, it typically wants single crystals of these materials. Whether we talk about an intrinsic semiconductor or whether we talk about an extrinsic semiconductor with dopants, we want an ideal single crystal with no defects. This is because, whenever you have polycrystalline material or if you have defects, so whenever you have polycrystals, you always have grain boundaries. Grain boundaries are source of defects. You could also have impurities, you can have vacancies, dislocations, all of these are defects in your crystal and whenever you have defects you always have defect states.

There are 2 types of defect states, one is shallow. Shallow states are those that are located either close to the conduction band or close to the valence band, so they close to the band edges. and, because they are close to the band edges, they can easily get ionized at room temperature. So, shallow states mostly affect the conductivity, can either increase or decrease the conductivity. The other type of defect states suppose to shallow states are deep states. So, deep states are states that are located much closer to the middle of the band gap or they are located far away from the valence band and the conduction band.

So, in this particular case, you have oxygen that is located approximately 400 milli-electron volts or 0.4 electron volts below the conduction band. So, deep states are located close to the center of the band gap. Deep states can essentially act as traps for electron and hole. So, they could modify the conductivity, especially in the case of direct band gap semiconductors, where we are looking at optical properties. Deep states can also act as traps for these electrons and volts and then decrease the efficiency of any optical recombination. We will see defect states later, when we also look at conductivity in an extrinsic semiconductor.

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E_F position in extrinsic semiconductor

$$E_{Fi} = \frac{E_g}{2} - \frac{1}{2} kT \ln\left(\frac{N_c}{N_v}\right) \quad n=p=n_i \quad E_{Fi} \text{ close to centre of gap}$$

Extrinsic $\Rightarrow n \neq p$

n-type

Fermi level position in n-type

$$n = N_d = N_c \exp\left[-\frac{(E_c - E_{Fn})}{kT}\right] \quad \text{--- (1)}$$

$$E_{Fn} - E_{Fi} = kT \ln\left(\frac{N_d}{n_i}\right)$$

$$E_{Fp} - E_{Fi} = -kT \ln\left(\frac{N_A}{n_i}\right)$$

p-type

$$p = N_A = N_v \exp\left[-\frac{(E_{Fp} - E_v)}{kT}\right] \quad \text{--- (2)}$$

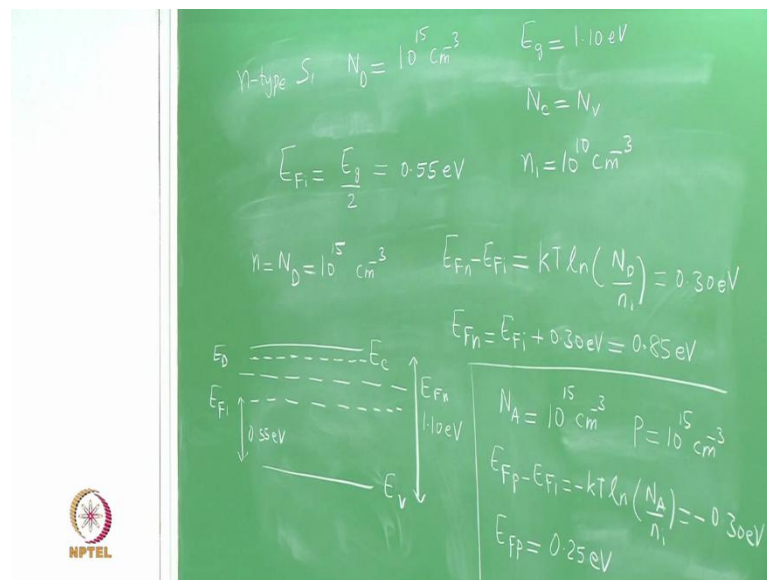
The next thing I am going to do is look at how the Fermi level position changes in an extrinsic semiconductor. So, we want to find out the position of E_F when you have dopants, whether you have p or n-type dopants. In the case of an intrinsic semiconductor, we have electron and hole concentration to be nearly the same. So, we wrote an expression for Fermi level position $\frac{E_g}{2kT}$. So, this is for the case of an intrinsic semiconductor, where $n = p = n_i$. And we found out that E_{Fi} is very close to the center of the gap. So, if N_c and N_v are exactly the same E_{Fi} will be just E_g over 2. But if they are not the same, it will be slightly shifted from the center of the gap, but for most cases it is very close to the centre.

In the case of an extrinsic semiconductor, n is no longer equal to p ; in fact, if we have an n-type semiconductor, we see that n is much larger than p ; if we have a p-type semiconductor, p is much larger than n . So, in order to compensate for this difference in n and p , the Fermi level will also shift from the middle. One way to look at it or to calculate the shift is to use the equation for the electron concentration. So, let me start with an n-type semiconductor with N_D being the concentration of the donors. The donors are all completely ionized, so the electron concentration same as the donor concentration. This we can write as $N_c \exp\left[-\frac{E_c - E_{Fn}}{kT}\right]$. So, E_{Fn} refers to the Fermi level position in the n-type semiconductor.

So, we can take this expression and then rearrange the terms a bit, and what we will get

is $E_{Fn} - E_{Fi}$ is nothing but $kT \ln \frac{N_D}{n_i}$. How we get this expression is that we start with this; we can write the same equation for intrinsic as $n_i = N_c \exp \frac{-E_c - E_{Fi}}{kT}$. So, we start with 1 and 2, and then we divide 1 and 2, and rearrange the terms to get the expression for the Fermi level position in an extrinsic n-type semiconductor with respect to the Fermi level position in an intrinsic semiconductor. Can write a similar equation for a p-type material as well, so you have $E_{Fp} - E_{Fi}$ which is $-kT \ln \frac{N_A}{n_i}$. So, the similar expression to this except that in an n-type, we have a concentration of the donors; in p-type you have concentration of acceptors, and there is a negative sign here. So, let us do some numbers to get a sense, where the Fermi level is located.

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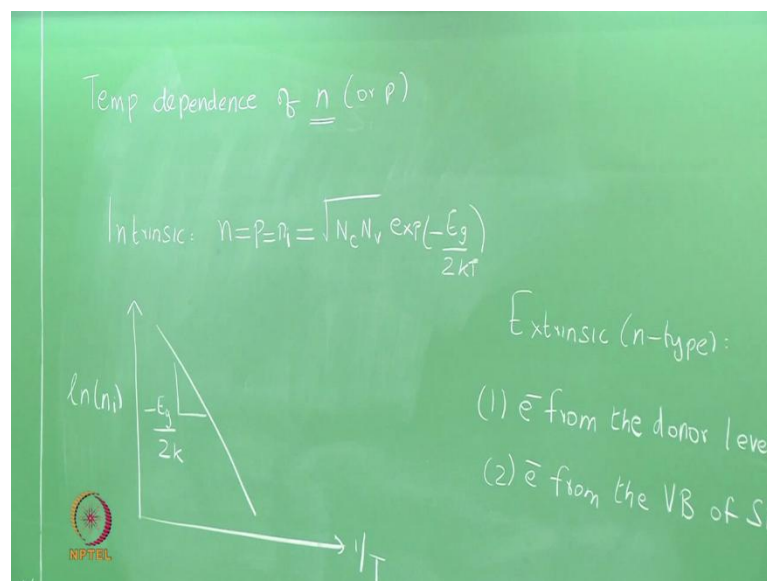


So, let us take n-type silicon with N_D is around 10^{15} cm^{-3} . We know the band gap of silicon E_g at room temperature is 1.10 electron volts. For simplicity, let us just say $N_c = N_v$. So, the intrinsic position of the Fermi level E_{Fi} will be just E_g over 2; we know this to be 0.55 electron volts. Now at room temperature, you have all the donor atoms are ionized, so $n = N_D = 10^{15} \text{ cm}^{-3}$. We will then use the formula that we just wrote down. So, that $E_{Fn} - E_{Fi}$ is $kT \ln \frac{N_D}{n_i}$. In the case of silicon, n_i is around 10^{10} , so substituting the numbers this gives you a value of around 0.30 electron volts or in other words E_{Fn} is $E_{Fi} + 0.30$ electron volts, which is $0.55 + 0.3 = 0.85$. Adding an n-type impurity, so or adding a donor shifts, the Fermi level above the intrinsic level.

If you want to show this in a band gap diagram, this is your valence band, this is the conduction band, and this is the band gap. So, this is 1.10 electron volts; E_{Fi} is located in the middle, so this is 0.55. So, you have added an n-type impurity. So, this creates the donor levels E_D . So, these donor levels are very close to your conduction band; at room temperature, all of the donors are ionized. And what we have is your Fermi level E_{Fn} located above the intrinsic level, but below your donor level. In the case of a p-type semiconductor, so let us do a situation where we have N_A , so it is a p-type just block it off with 10^{15} instead of electrons you have holes. So, your hole concentration is 10^{15} equation becomes $E_{Fp} - E_{Fi} = -kT \ln \left(\frac{N_A}{n_i} \right)$ which is -0.30 electron volts or E_{Fp} is 0.55 - 0.3 = 0.25 eV. So, in the case of a p-type semiconductor, you have the Fermi level located below the intrinsic level.

So, depending upon the type of extrinsic semiconductor you have, you can either have the Fermi level shift up, if we have more electrons which shift up towards the conduction band; if you have more holes, it shifts below towards a valence band. So, all these calculations that you have done so far is for an extrinsic semiconductor at room temperature, where all the dopants are ionized, whether there be donors or acceptors. So, the next thing we are going to do is to look at how the dopant constant or how the carrier concentration changes with temperature.

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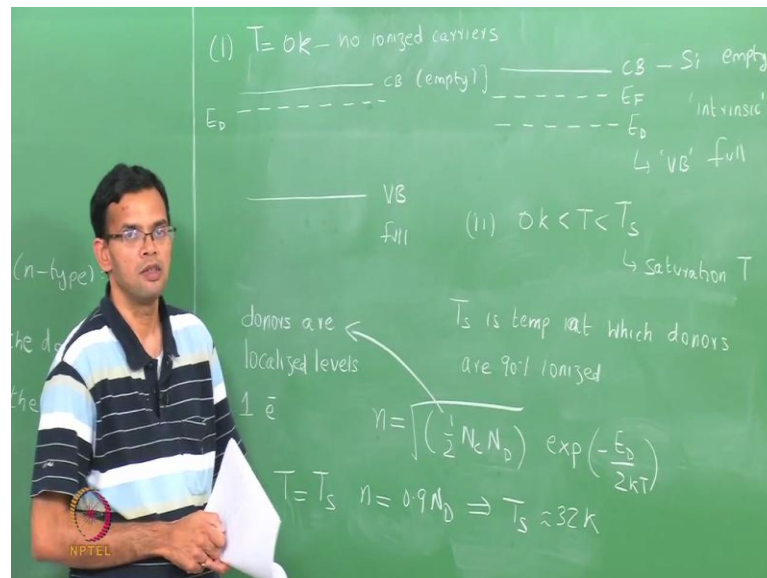


So, we want to look at the temperature dependence on the majority carrier concentration.

So, it is a temperature dependence of n , if it is an n-type; or p , if it is a p-type. For simplicity we have only going to look at the n-type case, but whatever arguments we use for that we can use the same for the p-type semiconductor. How is this different if you have an intrinsic semiconductor? In an intrinsic semiconductor, we have essentially no dopants. So, a carrier concentration $n = p = n_i$ was $\sqrt{N_c N_v} \exp \frac{-E_g}{kT}$. So, if you want to look at the temperature dependence of n , it is an exponential dependence on temperature. So, if you did a plot of the log of a carrier concentration over $1/T$, it is approximately a straight line as long as you assume that N_c and N_v are independent of temperature straight line with slope $-E_g$ over $2k$.

This is as far as an intrinsic semiconductor goes in the case of an extrinsic semiconductor again that is an n-type. You have essentially 2 sources for the electrons; you can get the electrons from the donor level, remember the donor atoms each have 1 more electron than the silicon that is why it is an n-type. So, you can get the electrons from the donor level, and you can also get the electrons from the valence band. So, because you have these 2 sources. So, we have a different behavior for how the value of n changes with temperature. We are going to look at different regimes for that.

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So, the first case, let us look at a semiconductor at exactly 0 Kelvin. So, in this case you have n-type semiconductors at 0 Kelvin, there are no ionized carriers. You have a valence band that is full, and you have a conduction band that is empty. And you also have a

donor level, because it is n-type which is also full. So, this is my condition band; this is my valence band, so that is full that is empty. And these are my donor levels; the donor levels are located very close to the conduction band. I am just exaggerating the difference to show the fact that they are close to the conduction band. We can expand this portion of the diagram, so that now I will draw the condition band, draw my donor level. At temperature equal to 0 Kelvin and a temperature is very close you going to have negligible number of electrons coming from the valence band. So, we can ignore the valence band totally, and think of this as an intrinsic semiconductor. So, I will put intrinsic within brackets, with the donor level acting as your valence band and the conduction band being the conduction band of silicon.

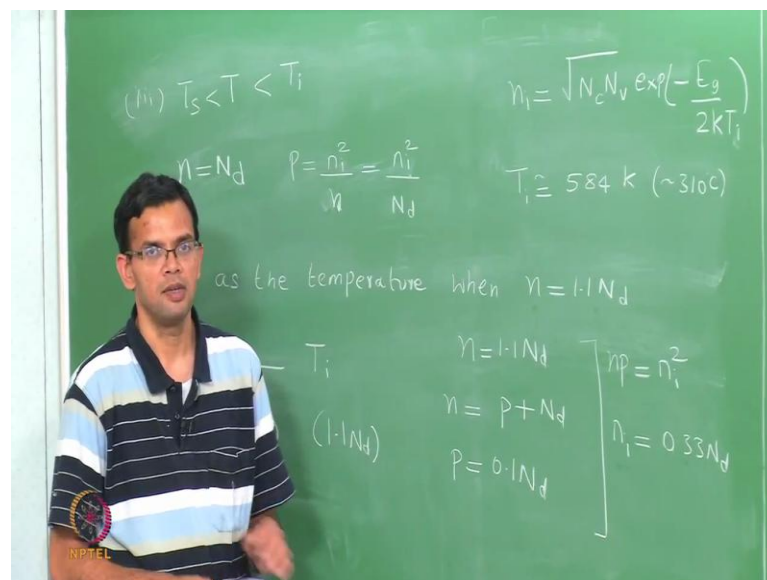
So, all I have done is just expand this portion here and take it to be an intrinsic semiconductor with the donor level being the valence band and **CB** being the conduction band of silicon. At room at 0 Kelvin you have a donor level that is completely full you have a conduction band that is empty and then you will have your Fermi level in between the conduction band and the donor level. Now, if you start to increase your temperature from zero Kelvin, electrons are going to get excited from the donor level to the conduction band. Once again your temperature is low enough that you can ignore any contribution from the valence band of silicon. So, we do this still some temperature which we are going to call **T_s** or a saturation temperature. So, a temperature is above 0 Kelvin, but it is below a certain temperature called **T_s** ; we are going to define **T_s** as saturation temperature.

In this particular regime, we are going to have electrons from the donor level getting ionized into the conduction band, and this process is going to happen till all the donors atoms are ionized. So, the saturation temperature is defined as the temperature in which the donors are 90 percent ionized. Some books will give you a definition of 99 percent ionized, but we will just use 90 percent here at which donors are. In order to calculate the value of **T_s** , we look at the expression for the electron concentration. We will treat this material as an intrinsic material with the donor level being your valence band. This case n is one-half **N_c** , instead of **N_v** you will have **N_D** which is your donor concentration **$\exp \frac{-E_D}{2kT}$** . The one-half term is here because your donor levels are localized levels, donors are localized levels. So, they can only take one electron.

A normal band can have 2 electrons of opposite spin because your donors are localized levels they can take only 1 electron which is why we have the term one-half. So, if we are treating this as an intrinsic with E_c being your conduction band and the donor being the valence band. and, at the saturation temperature, n is 90 percent of N_D . We can put this value here, and try and solve this expression for T_s . And if we do this, we get a value of T_s to be approximately 32 Kelvin. So, in this assumption, we take N_C to be independent of temperature; if we take in the temperature dependence of N_C , you will get T_s of around 60 Kelvin, but either way the number is much below room temperature which is around 300 Kelvin.

What this means is at a relatively low temperature in the case of silicon, you have a situation where the donors are completely ionized. So, we started at low temperature where we said that we will ignore all the electrons coming from the valence band, we found out that as we started going above 0 Kelvin, electrons are going to get ionized from the donor levels till we reach a saturation temperature when all most all the donors are ionized.

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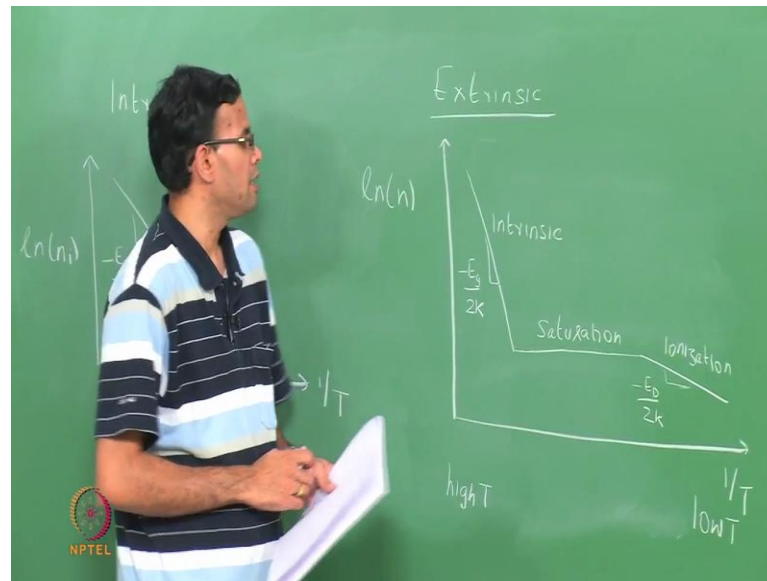
So, above the saturation temperature all the donor atoms are ionized, so that n is nothing but N_d and p would be $\frac{n_i^2}{n}$, which is nothing but $\frac{n_i^2}{N_d}$. Now if you keep increasing temperature further, there is going to come a point when electrons are starting to get ionized from the valence band. In this particular case, the semiconductor now behaves as

an intrinsic semiconductor, and we define this temperature as T_i . So, we define T_i as the temperature when $n = 1.1 N_d$. So, you have extra carriers that are now coming from the valence band of the silicon, and this makes it an intrinsic semiconductor. So, we had two temperatures T_s and T_i . So, T_s was $0.9 N_d$, T_i is $1.1 N_d$. So, we have a regime where the carrier concentration varies within 10 percent.

If you want to calculate the value of T_i the intrinsic temperature, we can look at the numbers. So, n is $1.1 N_d$, and we are going to treat this as intrinsic. In any semiconductor, the total charge should be balanced. So, $n = p + N_d$, so that p is 0.1 . We also know that $n p$ is n_i^2 . And then doing the math, we get n_i to be $0.33 N_d$. So, n is 10 percent more than your donor concentration; and at that temperature n_i is approximately $0.33 N_d$. We can use this expression $n_i = \sqrt{N_c N_v} \exp \frac{-E_g}{2kT}$, but now the temperature will be T_i which is your intrinsic temperature. You can substitute in the values once again, we will assume that N_c and N_v are independent of temperature that gives you T_i of approximately 584 Kelvin; if you try to convert that into degrees, this is approximately 310 degrees.

Above this temperature, a semiconductor essentially behaves as an intrinsic temperature. So, in the case of silicon, we have a regime starting from the saturation temperature which is around 50 Kelvin or 60 Kelvin; to an intrinsic temperature, there is around 584 Kelvin, where the carrier's concentration is essentially a constant. And, it is equal to the donor concentration; the difference is only within 10 percent. This means the conductivity will also be very stable because the conductivity depends upon the carrier concentration. If we put these numbers together, and did a plot of the log of the carrier concentration versus one over T , we can compare that to your intrinsic semiconductor.

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In the case of an intrinsic, you already done this before, log of n versus $1/T$ is just a straight line with 1 slope, so this is intrinsic. You can do the same for extrinsic. So, now instead of 1 slope, we will have 2 slopes, we have 3 regimes. In this particular case, since this is $1/T$, this is low temperature, this is high temperature. So, at low temperature, you have electrons coming from your donor level. So, you have a straight line with the slope that is given by your donor ionization. Then we have a situation where the donors were all ionized and a carrier concentration is almost a constant. At some high temperature, we are going to get new carriers from the valence band, the material behaves like intrinsic. So, this is $-\frac{E_g}{2k}$. So, we have three regimes - an ionization regime; a saturation regime, where the carrier concentration is almost a constant; and then finally, an intrinsic regime where the material starts to behave like an intrinsic semiconductor.

So, we will stop here for today. In the next class, we will look at how the conductivity changes as the function of temperature, and we also look at the effect of doping on the mobilities of electrons and holes.